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Biosorption of Eu(III) and U(VI) on *Bacillus subtilis*: Macroscopic and modeling investigation

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ABSTRACT

The biosorption of Eu(III) and U(VI) on *Bacillus subtilis* (*B. subtilis*) as a function of reaction time, pH, ionic strength, temperature was investigated by macroscopic and modeling techniques. The macroscopic experiments indicated that the biosorption kinetics and isotherms of Eu(III) and U(VI) on *B. subtilis* can be satisfactorily fitted by pseudo-second-order kinetic model and Langmuir model, respectively. No effect of ionic strength revealed that the inner-sphere surface complexation dominated the biosorption of Eu(III) and U(VI) onto *B. subtilis*. The maximum sorption capacity of *B. subtilis* calculated from Langmuir model at pH 4.5 and 298 K was 58.80 and 90.91 mg/g for Eu(III) and U(VI), respectively. According to the surface complexation modeling, the biosorption of Eu(III) and U(VI) on *B. subtilis* can be simulated by diffuse layer modeling with three inner-sphere surface complexation sites such as phosphoryl, carboxyl and hydroxyl groups. The findings presented herein suggested that *B. subtilis* is a promising bio-adsorbent for the preconcentration and retardation of radionuclides in the environmental remediation strategy such as permeable reactive barrier.

1. Introduction

The rapid development of nuclear-related industries (e.g., nuclear fuel production, weapons manufacturing) could be resulted in the radionuclide contamination in soils and aquifers [1]. The most remarkable pathway for human exposure to radionuclides is via groundwater transported away from such sites, which may be potentially harmful to both human health and the biodiversity of ecosystem [2]. Therefore, it is require us to remove these radionuclides within the scope of permissible concentration before discharge into subsurface environments.

Due to the ubiquitous occurrence and massive functional groups, *Bacillus subtilis* (*B. subtilis*) as gram-positive bacteria has been extensively investigated to remove a variety of environmental contaminants such as organics [3–6], heavy metals [7–11], radionuclides [12–15]. Gorman-Lewis et al. [13] found that uranyl species could form stable surface complexes on the cell walls of *B. subtilis* via electrostatic interactions and covalent bonding. In addition, Fowle et al. [12] determined that the neutral phosphate and deprotonated carboxyl functional groups of *B. subtilis* played important roles in the formation of uranyl complexes. Recently, extracellular polymeric substance (EPS) as heterogeneous biopolymers secreted by *B. sublitis* was easily combined with mineral surface through electrostatic and chemical bonding interactions [16]. However, the few studies towards the adsorption of radionuclides on *B. subtilis* by using surface complexation modeling [17–20].

The objectives of this study are (1) to characterize the morphology and functional groups of *B. subtilis* using scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and zeta potential (ζ) techniques; (2) to investigate the effect of water chemistry (i.e., reaction time, pH, ionic strength, temperature and initial radionuclide concentration) on U(VI) and Eu(III) adsorption on *B. subtilis* by batch techniques; (3) to determine interaction mechanism between radionuclides and *B. subtilis* according to surface complexation modeling. The highlight of this manuscript is that non-metallic reducing bacteria can be a promising bio-adsorbent to remove a variety of radionuclides from aqueous solutions in the environmental cleanup.

2. Materials and methods

2.1. Materials

B. subtilis was obtained from the College of Life Science at Sichuan University. *B. subtilis* cells were cultured in a beef extract-peptone medium at 303 K. Next, the cells were harvested by centrifugation (2776 ×*g*, 10 min) during the logarithmic phase and were washed three times using Milli-Q water. The U(VI) and Eu(III) stock solutions (0.1 mmol/L) were prepared from $UO_2(NO_3)_2 \cdot 6H_2O$ and $Eu(NO_3)_3$ (99.99% purity, Sigma-Aldrich) after dissolution and dilution with

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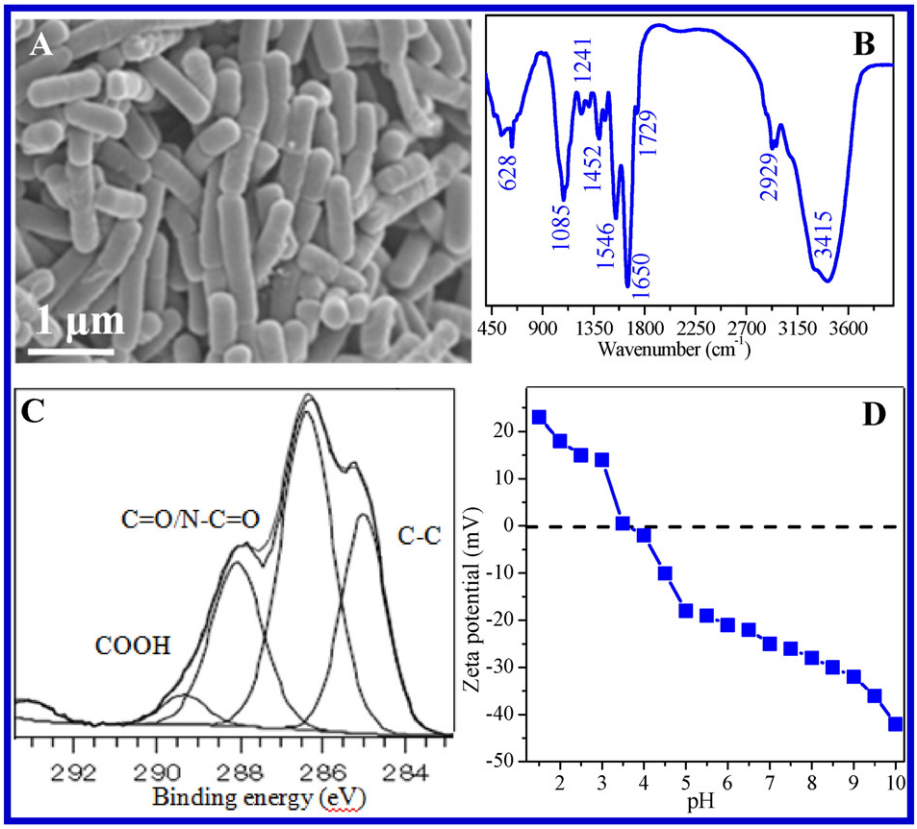

Fig. 1. Characterization of *B. subtilis*, A: SEM image; B: FTIR spectrum; C: XPS spectrum; D: zeta potentials.

0.01 mol/L HNO_3, respectively. The desired concentrations of radionuclides were diluted the aforementioned stock solutions before use. Other chemicals were commercially purchased as analytical reagents from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

2.2. Characterization

The morphology and functional groups of *B. subtilis* was characterized by SEM, FTIR, XPS, and zeta-potentials measurements. The SEM image was obtained using a field emission scanning electron microscope (FEI-JSM 6320F). The FTIR spectra were recorded in pressed KBr pellets (Aldrich, 99%, FT-IR grade) by using a Nicolet 8700 FT-IR spectrometer at room temperature. The XPS spectra were recorded on a thermo ESCALAB 250 electron spectrometer with multidetection analyzer using Mg Kα radiation source (1253.6 eV) at 10 kV and 5 mA under 10^{-8} Pa residual pressure. Surface charging effects were corrected with C1s peak at 284.6 eV as a reference. The recorded lines of C1s were fitted by using XPSPEAK41 program. The zeta potentials of *B. subtilis* at the different pH conditions were determined using Zetasizer NanoZS (Malvern Instruments). Five runs and ten cycles were set for each measurement. Each sample was measured at least three times.

Table 1
Selected physicochemical properties of *B. subtilis*.

Content (%)[a]	C—C (26.78%), C—O (52.48%), C═O (15.64%), COOH (5.16%)
S_{BET} (m^2/g)	88.53
V_{total} (cm^3/g)	0.451
Zeta potential	−20 mV at pH 5.0

[a] Determined by XPS analysis.

2.3. Batch adsorption experiments

The batch adsorption of U(VI) and Eu(III) on *B. subtilis* were conducted under ambient conditions. Briefly, 2 mL of 3.0 g/L *B. subtilis* suspension and 0.6 mL of 0.1 mol/L $NaNO_3$ were added into10 mL polycarbonate tubes, and then 1 mL of 60 mg/L U(VI) or Eu(III) solutions and 2.4 mL DI water were stepwise added into the aforementioned solutions. The pH of suspension was adjusted to 1.0–12.0 by adding the negligible volume of 0.01–1.0 mol/L NaOH or $HClO_4$ solutions, and then was agitated on a shaker for a reaction time of 24 h. The adsorption isotherms of U(VI) and Eu(III) on *B. subtilis* were performed at pH 4.5 and $T = 298$ K by batch technique. The experiments were conducted under the same conditions as the above pH-dependent adsorption experiments except that the different concentrations of radionuclides used. Subsequently the suspensions were shaken for 24 h to ensure that the adsorption reaction could achieve adsorption equilibrium (preliminary experiments found that this was adequate for the suspension to achieve equilibrium). The solid phases were separated from liquid phases by centrifugation at 9000 rpm for 10 min. To eliminate the effect of radionuclide adsorption on tube walls, the adsorption of radionuclides without adsorbents was carried out under the same experimental conditions. For all adsorption experiments, $^{238}UO_2^{2+}$ and $^{152\,+\,154}Eu^{3+}$ were used to tag the radionuclide nitrate stock solution. The radioisotope concentrations in suspensions were analyzed by liquid scintillation counting using a Packard 3100 TR/AB liquid scintillation analyzer (Perkin Elmer) with the scintillation cocktail (ULTIMA GOLD AB™, Packard). The amount of adsorbed radionuclides was determined from the difference between the concentration initially added and that remained after batch adsorption.